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W. J. Nellis

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Metallization and Dissociation of Fluid Hydrogen and Other Diatomics at 100 GPa Pressures

W. J. Nellis
University of California
Lawrence Livermore National Laboratory
Livermore, California 94550

Dynamic compression of diatomic liquids using both single-shock (Hugoniot) and multiple-shock (reverberating-shock) compression achieves pressures which range up to a few 100 GPa (Mbar), densities as high as tenfold of initial liquid density in hydrogen, and temperatures up to several 1000 K. Single-shock compression produces substantial heating, which causes a limiting compression. Multiple-shock compression is quasi-isentropic, which achieves lower temperatures and higher densities than single shocks, and has no limiting compression. Diatomic fluids have universal behaviors under dynamic compression. Under multiple-shock compression, these fluids undergo a density-driven nonmetal-metal Mott transitions with common density scaling. Under single-shock compression, these fluids have essentially the same Hugoniot in velocity space. D_2 undergoes temperature-driven dissociation to a poor metal at ~50 GPa. These results provide insight into which of the two published D_2 Hugoniots is probably correct.

Email: nellis1@llnl.gov

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I. Introduction

Hydrogen at ultrahigh pressures and temperatures in the fluid state is of great interest because of the condensed matter physics of these newly accessible extreme states of matter; for understanding interiors of the ~100 extrasolar planets which have been discovered; as fuel in the isotopic form of deuterium and tritium in inertial confinement fusion; and as a possible route to the synthesis of novel materials such as solid metallic hydrogen. Substantial interest in hydrogen has centered around its metallization, which was observed recently at 140 GPa, ninefold compressed initial liquid density, and ~2600 K achieved with a reverberating shock wave generated with a two-stage light-gas gun [1-5]. Similar results have been achieved with dynamic compression achieved with explosives [6]. At these conditions hydrogen is probably a fluid. Metallization of hydrogen has been a major scientific issue ever since it was predicted to undergo an insulator-metal transition at a pressure P of ~25 GPa at temperature T = 0 K [7].

Implications of measured equation-of-state (EOS) data and the nonmetal-metal transition in fluid hydrogen on the nature of Jupiter have been discussed [8-10]. Because hydrogen has a cosmological abundance of ~90 atomic percent, the ~100 extrasolar planets which have been discovered recently [11] can be assumed to be composed primarily of fluid hydrogen. Since their masses are typically 0.5 to 5 Jupiter masses [12], interior pressures and temperatures in these extrasolar planets are similar to those in Jupiter. Thus, considerations similar to those in [10] and EOS and electrical conductivity data over a wider range of pressures and temperatures achieved by multiple-shock compression are applicable to extrasolar planets.

Hydrogen in the form of a fluid mixture of deuterium and tritium is the fuel in inertial confinement fusion [13]. This fuel follows quasi-isentropes, paths which are similar to those achieved with multiple-shock compression starting from initial states on the Hugoniot [1-5].

If fluid metallic hydrogen could be retained metastably as a solid metallic glass on release of dynamic pressure, then a wide variety of novel materials would become available [14]. Of course, synthesizing metastable solid metallic hydrogen has substantial difficulties. One potential application is a room-temperature superconductor [15]. Another potential application is fuel for automobiles. General Motors is seeking a hydrogen-storage system to produce hydrogen for use in a fuel cell. The GM goal is hydrogen with a stored energy of ~12 MJ/kG [16]; present known research is investigating hydrogen-storage systems with 4-5 MJ/kG. The internal energy in metallic fluid hydrogen is ~120 MJ/kG. If this state could be retained metastably on release of dynamic pressure, then this energy would be available to do mechanical work by the controlled expansion from the metastable solid to the gas phase. The gasaeous hydrogen so produced would then be available for use in a fuel cell. Such a process would be a major technological advance.

The purpose of this paper is to discuss two major issues. The situation is illustrated in Fig. 1, which shows plots of pressure versus molar density of hydrogen and deuterium at various temperatures. These plots are the calculated 0-K isotherm of H_2 [17], the measured 300-K isotherm [18], the quasi-isentrope on which hydrogen undergoes a nonmetal-metal transition [2], and two different measured Hugoniots. The D_2 Hugoniot in [19] differs substantially from the one in [21,22]. Two issues are discussed below: (i) the nature of the density-driven nonmetal-metal transition at 140 GPa on the quasi-isentrope and (ii) which of the two Hugoniots of D_2 is probably correct.

II. Density-driven Nonmetal-metal Transition

The observed nonmetal-metal Mott [23] transition in dense fluid hydrogen, achieved with multiple-shock compression generated with a two-stage gun, has been discussed extensively [1-5]. The metallic state is achieved because pressure reduces the 15 eV mobilty gap E_g and thermal disorder fills it in until the mobility gap is filled in completely and the electronic system has a Fermi surface. Since $T \sim 2T_M$, where T and T_M are the calculated temperature and melting temperature, respectively, the system is probably in the fluid state. The condition on the Hugoniot for temperature-driven dissociation to a monatomic metallic fluid is $k_B T_d / E_d \sim 0.1$, where k_B is Boltzmann's constant, T_d is dissociation temperature, and E_d is dissociation energy at the density of dissociation [24]. Since this condition is also essentially the case for density-driven metallization at more than twice the Hugoniot density and since calculated dimer lifetimes are $\sim 10^{-14}$ s [25], it is quite likely that metallic fluid hydrogen is monatomic. Since the time between interatomic collisions is $\sim 10^{-14}$ s and the time resolution of the resistance measurement is $\sim 10^{-9}$ s, the fluid is in thermal equilibrium.

Metallization density of H is calculated to within a few % by the Herzfeld criterion [26], which depends only on the polarization of the free atom. Thus, interactions are relatively weak, which implies that the free-electron picture is reasonable to estimate the Ferm Energy E_F. At metallization density and one electron per atom, E_F ~ 20 eV. Thus, T/T_F ~ 0.01 and the system is highly degenerate, as well as disordered. It is disorder which probably causes the metallic state at a lower pressure (140 GPa) than for the solid. Metallization of the crystal is predicted to occur somewhat above 400 GPa [27], though it is yet to be observed.

Conduction electrons have a very short mean free path of ~2A. This is a strong-scattering system characteristic of minimum electrical conductivity of a metal. Fluid Cs, Rb, and H and O at ~2000 K metallize with a conductivity of 2000 $(\Omega\text{-cm})^{-1}$ with similar density scaling. The results for H, O [28], Cs, and Rb [29] are plotted in Fig. 2. Results for N [30] are similar to those for O. Thus, a density-driven Mott transition occurs systematically in H, O, N, Cs, and Rb. In contrast water is a proton conductor at these pressures [31].

III. Which is the Correct Hugoniot of Deuterium?

Two different D_2 Hugoniots have been measured recently at 100 GPa pressures and temperatures of several 1000 K [19,21,22], as seen in Fig. 1. These Hugoniots have limiting compressions which differ by ~50%, a substantial discrepancy. This difference has been controversial [24] and a key question is which D_2 Hugoniot in Fig. 1, if either, is probably correct?

D_2 Hugoniot measurements at 100 GPa require extremely large facilities. Da Silva et al [19] used the Nova Laser and Knudson et al [21] used the pulsed-current Z Machine. Trunin et al [22] reported a preliminary Hugoniot point using a converging shock wave generated by high explosives. Deuterium in all these experiments is in thermal equilibrium because the time between interatomic collisions is $\sim 10^{-14}$ s and experimental resolution is 10^{-10} s. Thus, there are $\sim 10^4$ atomic collisions within the time resolution.

The two Hugoniots in Fig. 1 have limiting shock compressions of 6-fold [19] and 4-fold [21,22] of initial density. Six-fold compression was ascribed to dissociation [32]. Since limiting shock compression of an ideal monatomic gas is four-fold [33], the data of Knudson et al suggest that D_2 is dissociating into atoms. Higher limiting compression is possible only if the diatomic molecule is maintained intact. Thus, significant insight into the critically important issue of dissociation is available immediately through comparison with other diatomic systems by comparing shock velocity u_s and residual mass velocity u_p behind the shock front. Because shock temperatures are several 1000 K and quantum effects are negligible at high temperatures, D and H are expected to behave as their heavier neighbors in the Periodic Table.

The Hugoniots of diatomic molecules have a common, systematic behavior in u_S-u_P space, as illustrated in Fig. 3 for D_2 [21,22,34], H_2 [34], N_2 [35-37], CO [38], and O_2 [35] up to u_p = 18 km/s. The solid line is the fit to the D_2 data [34]; the dashed line is its linear extrapolation. Figure 3 illustrates that the u_s-u_p data of these diatomic fluids lie on a common line, dissociation of CO, N_2, and D_2 is observed as a slight decrease in u_s (~3%) relative to this line, and u_s then increases as dissociation completes. The data of ref. [19] (not shown) deviate significantly from this universal behavior; values of u_p are in the range 18 to 32 km/s and values of u_s are ~7.5 % lower than the dashed line. Figure 3 emphasizes that very high experimental accuracy is required to characterize dissociation.

By transforming the u_s-u_p relations in Fig. 3 via the Hugoniot equations, data of deuterium, hydrogen, nitrogen, carbon monoxide, and oxygen are plotted as shock pressure versus relative compression in Fig. 4. Although oxygen dissociates above 30 GPa, it is not apparent because its density change and dissociation energy are small relative to those of N_2 [39]. An important point here is that relatively small variations in u_s-u_p space cause substantial variations in P-V space.

Above ~60 GPa D, N, O, and C+O asymptotically approach 4-fold compression, limiting shock compression of an ideal monatomic gas. At the densities and temperatures of these data, pressures are definitely not ideal. However, the systematic approach to 4-fold compression is strong evidence that dissociation to atoms is becoming complete and that average kinetic energy dominates average potential energy above ~60 GPa. Because a classical ideal gas has a limiting shock compression and a degenerate electron gas does not, the approach to 4-fold compression must be a direct consequence of the monatomic character of the species present above ~60 GPa. Below ~30 GPa D_2, H_2, N_2, O_2, and CO are diatomic and thus dissociate between ~30 and ~60 GPa.

Evidence for the complete dissociation of D_2 at a shock pressure of ~50 GPa is provided by the temperature data which plateaus at ~0.5 eV near 50 GPa [40]. This plateau is characteristic of a latent heat of dissociation, as in nitrogen [36], and indicates that dissociation is temperature-driven. Optical reflectivities of deuterium also indicate dissociation is complete by ~50 GPa. Reflectivities increase from <0.1 at 20 GPa up to saturation at ~0.5 at shock pressures above 50 GPa [41]. A reflectivity of 0.5 is characteristic of a poor metal and, thus, dissociation to a monatomic state is accompanied by a nonmetal-metal transition. Because virtually no molecules exist above 50 GPa, it is unlikely that six-fold compression can be attributed to dissociation.

The above analysis indicates that fluid D_2 undergoes a diatomic-to-monatomic transition at 0.6-0.7 g/cm^3, 5000-10000 K, and ~ 50 GPa on the Hugoniot, in excellent agreement with recent predictions [42]. Dissociation does vary with density and temperature, which are different off the Hugoniot.

In conclusion, the data of Knudson et al are probably correct because they agree with the universal behavior of diatomic liquids (Fig. 3). It is very unlikely that this agreement would occur accidentally with inaccurate data. The corresponding pressure-compression curves (Fig. 4) are approaches to monatomic ideal gases. The fact that D has no core and is a light, potentiallyquantum atom is of no consequence at the high temperatures on the Hugoniot. D behaves as its heavier neighbors in the Periodic Table.

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Figure Captions

Fig.1 Pressure versus molar volume of H_2/D_2 at various temperatures (solid line: 0-K isotherm of H_2 [17]; squares: 300-K isotherm of D_2 (open) and H_2 (solid) [18]; circles: quasi-isentrope of H_2 (open) and D_2 (solid) [2]; diamonds: Hugoniot of D_2 (solid) and double shock of D_2 (open) [20]; inverted triangles: Hugoniot of D_2 (solid [21] and open [22]); solid triangles: Hugoniot of D_2 [19].

Fig. 2 Conductivities versus cube root of number density of atoms times effective Bohr radius: Cs (x); Rb (+); H (triangles); O (circles). After [29]

Fig. 3. Hugoniots plotted as u_s versus u_p of deuterium (open circles [21]; solid diamond [22]; solid circles [34]), hydrogen (open inverted triangles [34]; nitrogen (open squares [37]; solid squares [35,36]; carbon monoxide (solid triangles [38]); and oxygen (solid inverted triangles [35]. Solid line is fit to D_2 data [34]; dashed line is its extrapolation. Dissociation of D_2, N_2, and CO is observed as slight decrease in u_s (~3 %) from line. Deuterium data in [19] (not shown) have values of u_p in range 18 to 32 km/s and u_s values ~7.5 % below dashed line.

Fig. 4. Hugoniots plotted as pressure vs relative compression (ρ/ρ_0). Symbols are same as in Fig. 3. Curves were calculated with Hugoniot equations and fits to u_s-u_p data in Fig. 3, except for guide to eye through open circles.

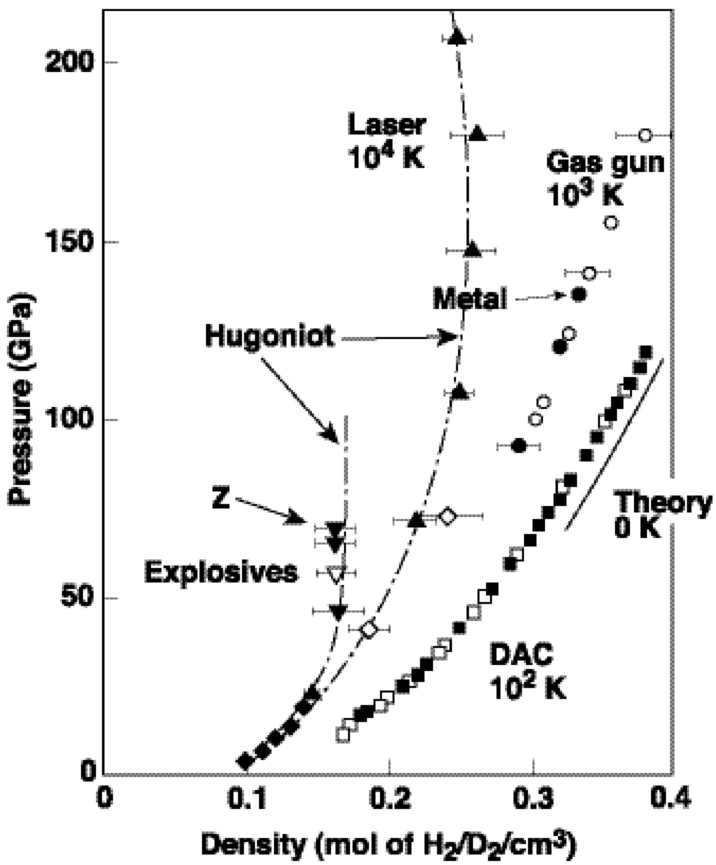

Fig. 1 Nellis

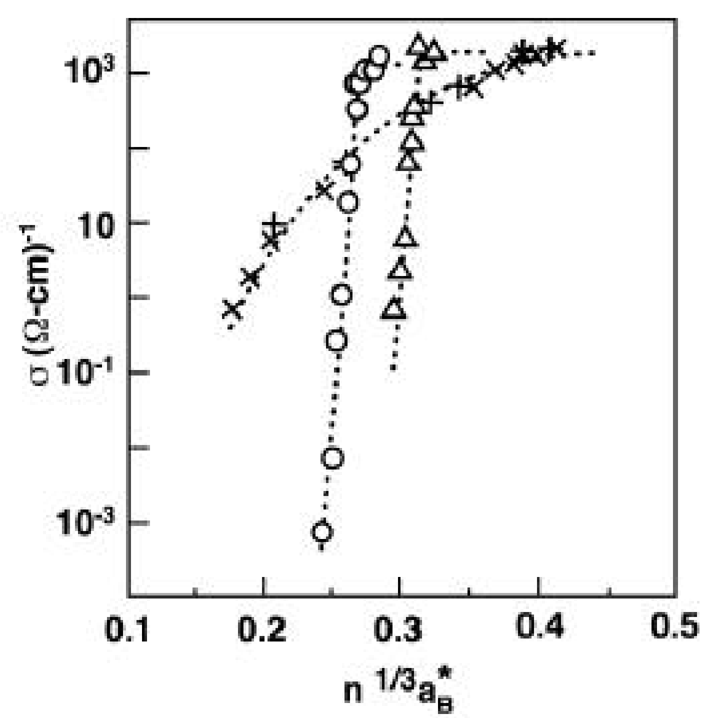

Fig. 2 Nellis

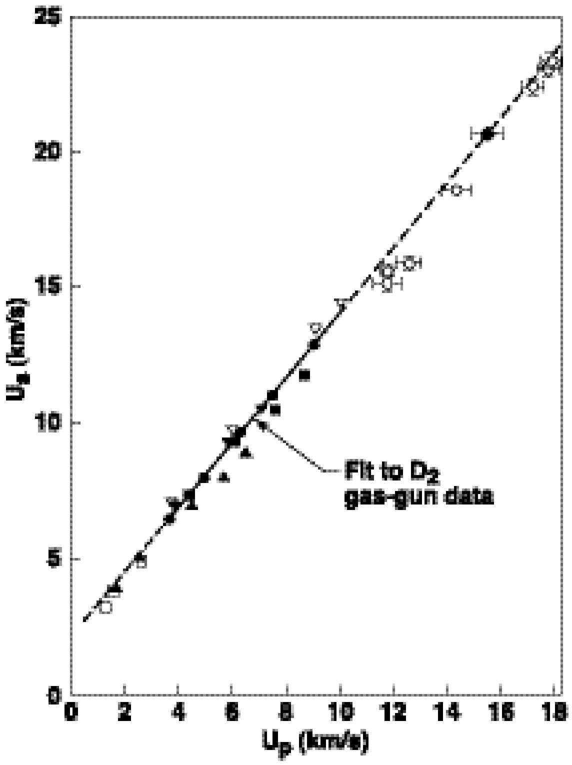

Fig. 3. Nellis

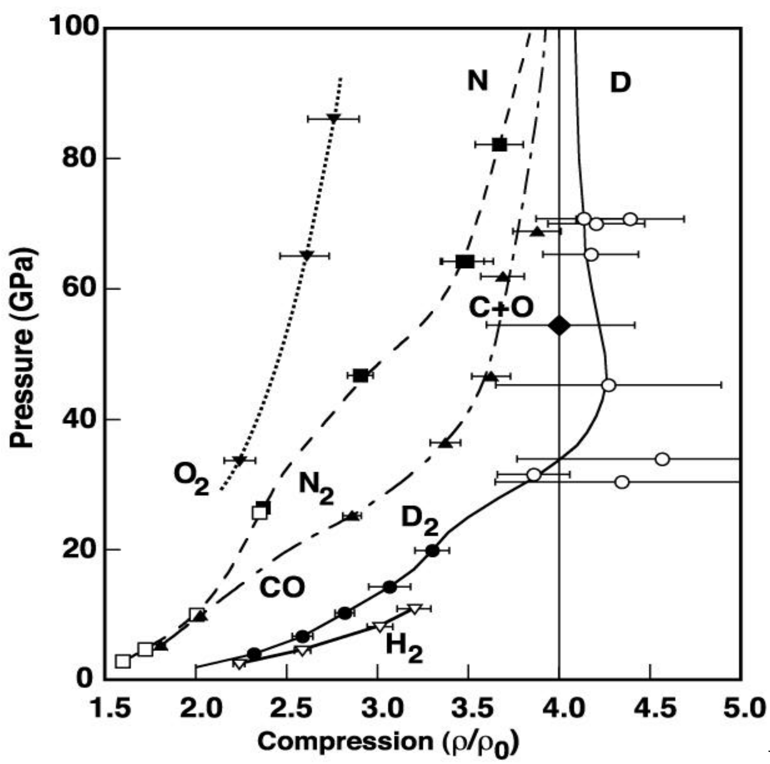

Fig.4. Nellis